Characterization of Acrylonitrile Grafted onto Pineapple Leaf Fibers Using Hydrogen Peroxide as an Initiator.

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ABSTRACT

Pineapple fiber obtained from the pineapple leaf, was grafted with acrylonitrile for used as textile. The leaf is first defatted to remove the organic matters and graft copolymerized with acrylonitrile. Hydrogen peroxide in combination with Fe^{2+} is used as an initiator during the graft copolymerization process. Acrylonitrile was grafted onto the pineapple leaf fiber (PALF) at various time intervals to determine the degree of grafting with respect to the copolymerization times. Characterization of grafted PALF is determined for the degree of grafting on the Fourier Transform Infra-Red Spectroscopy and thermal characteristics is analyzed on the thermogravimetric analysis (TGA). The grafted PALF shows an additional band at 2358 cm^{-1} until 2700 cm^{-1} indicative of nitrile group. The optimum time for acrylonitrile grafting is 5 hours with hydrogen peroxide concentration of 2 mol L^{-1} and 0.1 g of Fe^{2+} at 60 °C. Thermal stability of the grafted PALF showed enhancement, with respect to grafting and ranges between 230 to 380 °C.

Keyword: graft copolymerization; acrylonitrile; pineapple leaf fibers;

1. INTRODUCTION

The present day research in the field of polymer science technology has been focused in developing plastics, papers, adhesive, textiles fibers, composites, blends, and many other industrial products from renewable resources, mostly the abundantly available agro-waste and lignocellulosic materials (Jian *et al.*, 2006). This is expected to minimize the use of expensive synthetic polymers and fibers of petrochemical and mineral origin. However, in Malaysia, this area of research is still at its infancy.

The natural fibers are strong, light in weight, abundant, non-abrasive, non-hazardous and inexpensive, which can serve as an excellent textiles performance (Bledzki *et al.*,1996, 1999). Over the past decade cellulose-based natural fibers have found use as a potential resource. Cellulose-based natural fibers are used for low-cost composite materials and use in textiles field to enhance many needed properties such as tensile strength, drying rates ability, insect resistance and many others properties (R. E. Fornes and R. D. Gilbert, 1992 & Narendra *et al.*, 2004, 2005).

2. MATERIALS AND METHODS

2.1 Materials

PALF was collected from Pontian, Johor, Malaysia. The defatted PALF was obtained after successive extraction procedures. Analytical reagent grade hydrogen peroxide was purchased from Riedel-de-Haen (Germany) and Ammonium ferrous (II) sulphate was obtained from BDH (England), and used

as received. The acrylonitrile solvents and other chemicals of analytical grade were used as received. The fibers were first subjected to Soxhlet extraction with acetone for 24 h. After that, the fibers were washed with distilled water and sun-drying. Then, the fibers were extracted in a 1:2 mixture of methanol and benzene for 16 h to dewax followed by washing with distilled water and oven-drying to obtain the defatted PALF for grafting.

The AN monomer was washed with 5 % NaOH and 3% orthophosphoric acid followed by deionized water, dried over anhydrous calcium chloride and finally stored in a refrigerator. The deionized water was used for the preparation of all solutions. A solution of H_2O_2 was prepared by dissolving the required quantities of H_2O_2 in the conductivity water.

2.2 Graft Copolymerization

The reaction was carried out in a 250-ml-three-necked flask with reflux condenser and nitrogen inlet tube. About 0.1 gram of defatted PALF was added to 100 ml of distilled water. The flask was immersed into a thermostat water bath at required temperature. The nitrogen gas was purged into the flask for 30 minutes before reaction to remove the oxygen. After 30 minutes, 2.0 M H_2O_2 was added and allowed to react with substrate for 5 minutes followed by the addition of ammonium ferrous (II) sulphate. Then, acrylonitrile was added into the mixture and stirred continuously at varying reaction period (two until five hours). After each reaction period, the products were filtered, washed thoroughly with distilled water and dried in an oven at 60 °C to constant weight, method used by Ibrahim *et al.* (Ibrahim *et al.*, 2003) for grafting methyl methacrylate onto oil palm empty fruit bunch fiber.

The grafted PALF was purified from homopolymer by soaking a crude product in dimethylformamide (DMF) for 24 hours. The grafted products were then dried in an oven at 60°C to constant weight.

2.3 FTIR

Perkin-Elmer Model Fourier Transform Infra Red (FTIR) was used to investigate the chemical structure to determine the polymer bonding and interactions. Background scanned was done prior to analysis to ensure no disturbances exist which will influence the results. Scanning was carried out from 370 to 4000 cm^{-1} according to ASTM E 2105-00.

2.4 Thermogravimetric Analysis (TGA)

Thermal stability of the samples was examined on a Perkin-Elmer Thermogravimetry Analyzer TGA7. The analysis was carried out in N_2 atmosphere from 30 °C to 950 °C at heating rate of 10 °C min^{-1} with an N_2 flow rate of 20 mL^{-1} according to ASTM E 1131-03.

3. RESULTS AND DISCUSSION

3.1 Effect of Reaction Period on Percentage of Grafting

The graft copolymerization was carried out for various reaction times in a constant condition using H_2O_2 ; 2.000 mol L-1, Fe^{2+} ; 0.1 g, AN; 0.719 mol L^{-1}, and temperature ; 60 °C. The percentage of grafting is determined from the absorption intensity in the FTIR by the nitrile group was used to observe the trend of grafting. The losses of carbonyl group (C=O) was carried out to calculate how many carbonyl (C=O) was lost which is substituted with nitrile (C≡N) onto PALF.

3.2 Loss of Carbonyl (C=O) Group

The absorption intensity of carbonyl group loss during substitution was used to explain the trend of grafting. From the FTIR spectra, it showed that the peaks at 1710 cm^{-1} decreased due to the increment of reaction times. The absorption intensity of carbonyl (C=O) decreases because AN was substituted and grafted at this site. The decrement of carbonyl showed the increased in AN attached at the site which contribute to the increment in the degree of grafting. As the AN attached at carbonyl (C=O) group, the same occurrence was assumed to be at the hydroxyl group.

Figure 3.1 illustrates the absorption peak of C=O, at 1710 cm^{-1} varies in the absorption intensity. As the time of grafting reaction increases the intensity of the C=O absorption peak is decreased as summarized in Table 3.1. The peak intensity indicates that it is dependent on the losses of carbonyl group which had been substituted with nitrile (C≡N) group.

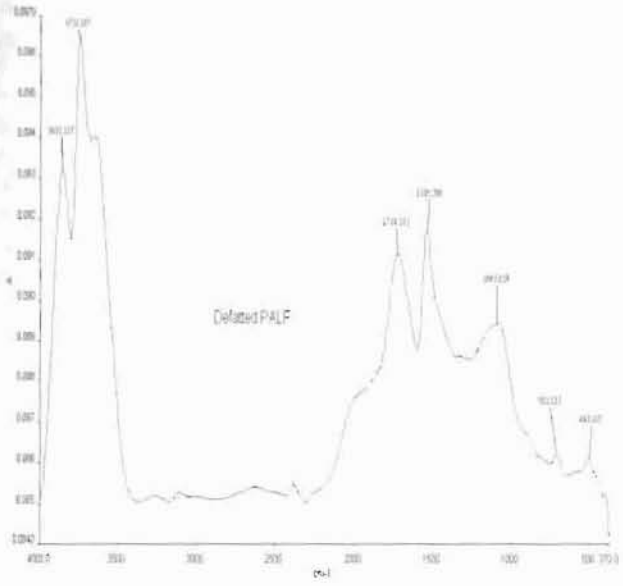


Figure 3.1 The absorption spectra for ungrafted PALF

The absorption peaks of carbonyl group showed the decrement with respect to the carbonyl absorption peak before grafting. This was probably due to the AN grafted onto PALF in form of many short chains or a long chain which cannot be determined with FTIR or absorption spectra (Magdy, 2006).

Table 3.1 Loss of Carbonyl Group for Various Grafting reaction time.

Time of reaction (hours)	Height of carbonyl band
0	0.0063
2	0.0059
3	0.0052
4	0.0029
5	0.0024

Temperature 60°C, H_2O_2; 2 mol L^{-1}, Fe^{2+}; 0.1 g, monomer (AN); 0.759 mol L^{-1}

The longer the reaction time the more AN got grafted onto the PALF from the higher losses of carbonyl group in PALF observed via the decrement of intensity of carbonyl peak. This indicated that more nitrile group attached onto the PALF. The highest lost of carbonyl group is after 5 hours of grafting time which correspond to the highest grafting of AN onto PALF.

The same weight of AN grafted onto PALF may correspond to either a few long branches or many short ones. The physical properties of these two types of grafted copolymer are not the same. Thus, it is important to calculate the number of grafted branches per cellulose backbone chain.

3.3 Propose Reaction Mechanism of AN Grafted onto PALF

The graft copolymerization of AN onto PALF was carried out by treating PALF with H_2O_2 and ferrous ammonium sulphate solution and AN. The proposed mechanism used in this study based on the same principles as that used by Ibrahim (Ibrahim *et al*,2003, Patra *et al.* 1994). However, the AN were attached at hydroxyl (-OH) and carbonyl (C=O), the mechanism of grafting of AN onto PALF would be the same. The first step in the mechanism is the generation of radicals by the decomposition of H_2O_2. According to Samal *et al.*, (Samal *et al.* 1994) the decomposition of H_2O_2 into radical is difficult to occur, so that Fe^{2+} was added to speed up the decomposition. The radical species HO• may attack the cellulosic hydroxyl to produce macroradicals. The Fe^{3+} will react with the phenolic hydroxyl group of lignin to produce macroradicals and ferrous ion. Samal *et al.* (Samal *et al.*, 1996) and Ibrahim *et al.* (Ibrahim *et al.*, 2003) have developed the following reaction Scheme 1 for the decomposition of hydrogen peroxide in the presence of Fe^{2+}. The cellulosic radicals and phenolic radicals may then react with AN monomer to initiate graft copolymerization. In the presence of vinyl monomer, the PALF free radical is added to the double bond of vinyl monomer resulting in a covalent bond between monomer and PALF fiber to create the chain reaction for propagation. The termination of graft copolymerization is through combination of two radicals and producing homopolymer and copolymer.

Initiation :

$H_2O_2 \rightarrow 2HO\bullet$

$H_2O_2 + Fe^{2+} \rightarrow HO^- + HO\bullet + Fe^{3+}$,

$HO\bullet + Fe^{3+} \rightarrow HO^- + Fe^{2+}$

The HO• radicals further decompose H_2O_2

$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$,

$HO_2\bullet + H_2O_2 \rightarrow HO\bullet + H_2O + O_2$

Propagation:

Cellulose — OH + HO • → Cellulose — O• + H_2O

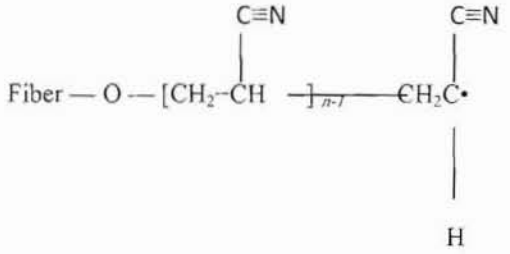
At the same time,

Lignin— OH + OH^- → Lignin— O^- + H_2O

Lignin— O^- + Fe^{3+} → Fe^{2+} + Lignin— O•

Termination:

Fiber — O• + n [H_2C=CHC≡N] →



Scheme 1: Propose mechanism of graft copolymerization of AN onto PALF

3.4 Analysis of FTIR Spectra

FTIR spectra of ungrafted PALF, defatted PALF and that of AN grafted PALF are shown in Figure 3.2. The FTIR absorption pattern of parent PALF shows bands at 3847 cm^{-1} and 3726 cm^{-1} due to –OH groups, 1710 cm^{-1} due to C=O stretching of hemicellulose, 1526 cm^{-1} due to C-C stretching, 1061 cm^{-1} broad band due to C-O/C-C stretching. The defatted PALF also has the same FTIR absorption pattern. FTIR spectra of AN-grafted PALF for all reaction period were observed to contain an additional band at 2358 cm^{-1} until 2700 cm^{-1} for nitrile group confirming the occurrence of AN grafting. Similar results were obtained for AN-grafted PALF for other initiator systems such as (Mohanty *et al.*,1999) using periodate as initiator.

In FTIR spectra analysis, the absorption peaks pattern at 1710 cm^{-1} due to carbonyl (C=O) stretching of defatted and AN-grafted PALF showed the decrement in the intensity with respect to the increment of reaction time which became broader and less intense. Similar trend is observed for the peak at 3700 cm^{-1} due to –OH group. Thus from this spectra, the grafting occurred at both the hydroxyl and carbonyl sites which is being substituted by nitrile (C≡N) group from AN. There were two probabilities would occur on the PALF backbone; a long chain of nitrile or many short chains of nitrile attached to the backbone which cannot be determined by FTIR analysis.

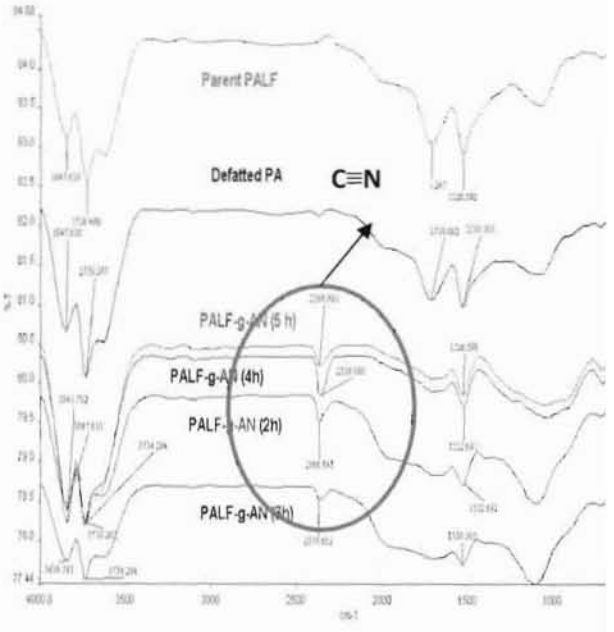


Figure 3.2 Infra Red Spectra of ungrafted PALF and ungrafted PALF

3.5 Thermogravimetry Analysis (TGA)

The thermal behaviour of ungrafted PALF as well as of AN-grafted PALF was examined by thermogravimetric analysis (TGA). The TGA curves of the original PALF and AN-grafted PALF are shown in Figure 3.3. It is observed that grafting has improved the thermal stability of PALF. In Figure 3.4(a), the decomposition for ungrafted PALF ranges from 150-450°C, amounting to 89.682% weight loss. The

decomposition of AN-grafted PALF after 5 h reaction period, ranges from 250-500°C, amounting to 92.212 % weight loss, as indicated in Figure 3.4(b) which showed the highest thermal stability. The incorporation of AN onto PALF via grafting method has increased the thermal stability of PALF. Thermal stability also increases with grafting time indicating the higher the AN content the higher is the thermal stability of PALF. Figure 3.5 showed the onset decomposition temperature verses reaction times. The increment of onset decomposition temperature with respect to reaction time is because of the increment of nitrile substitution which results in the lost of carbonyl group thus making the reaction with oxygen more difficult. This probably due to the less polar nitrile group compared to carbonyl that affect the oxidative process. This is also related by Ibrahim *et al.* saying that the increase in thermal stability in AN-grafted PALF may due to AN having higher stability, thus increasing overall thermal stability in AN-grafted PALF (Ibrahim *et al.*, 2003, Varma et al., 1971). Whereas Das et al. concluded that the increment is probably due to the fact that the grafted polymer entangled and form a crosslinked type of network, which when heated forms an insulative carbonaceous char barrier on the surface, thus inhibiting degradation (Das *et al.*, 1999).

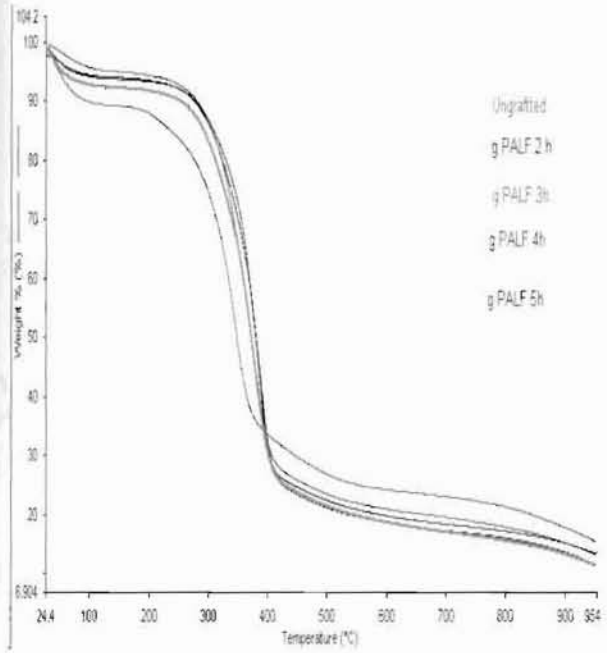


Figure 3.3 TGA curve of ungrafted PALF and PALG-g-AN in various period of time reaction

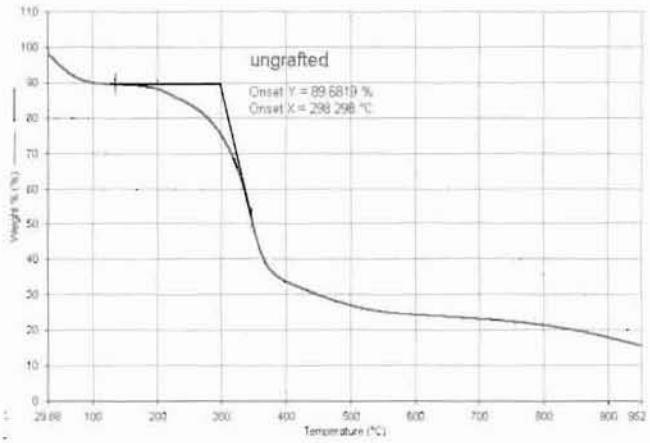


Figure 3.4 (a) TGA curve of ungrafted PALF

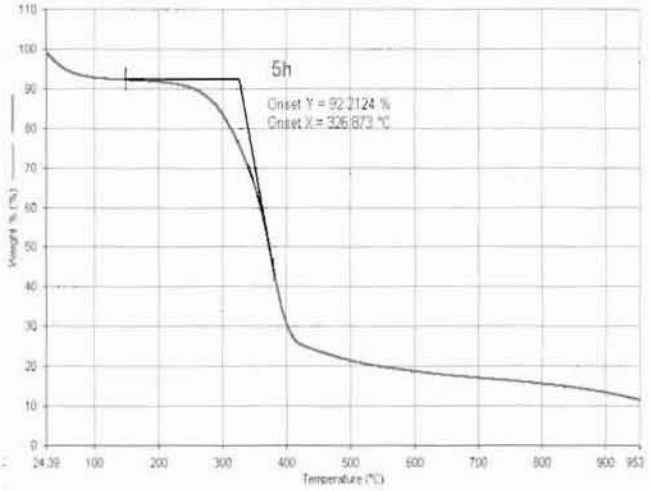


Figure 3.4 (b) TGA curve of 5 hours period of grating reaction.

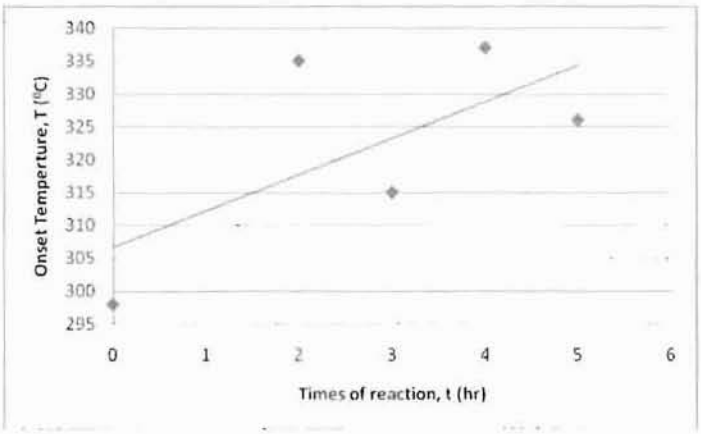


Figure 3.5 Degree of Temperature verses Times for grafting

4. CONCLUSIONS

From these studies, it is concluded that a combination of H_2O_2 and Fe^{2+} as hydroxyl initiator in an aqueous medium with hydrogen peroxide concentration of 2.000 mol L-1 and Fe^{2+} at 0.1 g with a fiber-to-liquor ratio of 1:50 at 60° C gave the highest grafting after reaction time period of 5 hours. Grafting occurs at the carbonyl group and also at the hydroxyl group on PALF. Grafting improves the thermal stability of PALF and increases with the degree of grafted acrylonitrile.

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